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Multifunctional nanofibers comprised of conducting and ferroelectric polymer composites

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Nicholas Pinto, Luis Rosa

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14. ABSTRACT
Work on this proposal concentrated on studying the following polymers: poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE); poly(3-hexylthiophene) (P3HT); poly(3,4-ethylenedioxthiophene) doped with poly-styrene sulfonic acid (PEDOT-PSSA); and (poly[N,N?-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyll-alt-5,5?-(2,2?-bithiophene)]-[P(ND12OD-T2)]n. We used the Langmuir Blodgett technique to prepare thin films and electrospinning to prepare fine fibers of these polymers. The goal was to make devices and sensors. Using an

15. SUBJECT TERMS
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UU	UU	UU	UU		Nicholas Pinto
					19b. TELEPHONE NUMBER
					787-850-9381

Report Title

Multifunctional nanofibers comprised of conducting and ferroelectric polymer composites

ABSTRACT

Work on this proposal concentrated on studying the following polymers: poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE); poly(3-hexylthiophene) (P3HT); poly(3,4-ethylenedioxthiophene) doped with poly-styrene sulfonic acid (PEDOT-PSSA); and (poly[N,N?-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyll-alt-5,5?-(2,2?-bithiophene)]-[P(ND12OD-T2)]n. We used the Langmuir Blodgett technique to prepare thin films and electrospinning to prepare fine fibers of these polymers. The goal was to make devices and sensors. Using an atomic force microscope we were able to make cuts into the fibers (nano-shaving) and record the current-voltage characteristics of the cut fiber. The results show the onset of an electronic gap as the cuts progress into the fiber. Field effect transistors were also prepared and used as UV sensors and also the device performance improved under UV illumination. The work was carried out by several undergraduate students and one graduate student. Students were involved in many poster presentations at scientific conferences and in refereed publications. State of the art equipment was also purchased making our laboratory competitive for undergraduate institutions. The following report summarizes the various projects that were undertaken over the three year period of this project.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
07/25/2014	6.00	Pablo I. Sepulveda, Alexander O. Rosado, Nicholas J. Pinto. Dielectric spectroscopy of [P(NID2OD-T2)]n thin films: Effects of UV radiation on charge transport, Thin Solid Films, (07 2014): 0. doi: 10.1016/j.tsf.2014.07.007
07/25/2014	8.00	Alexander O. Rosado, Nicholas J. Pinto. Electrospun fibers of [P(ND12OD-T2)]n on p-doped Si: Fabrication of a sub-micron size p-n junction diode, INTERNATIOal Journal of Chemcial Engineering, (07 2013): 0. doi:
08/07/2012	2.00	David Delgado, Freddy Wong, Omar Vega, Rosette Gonzalez, Luis G. Rosa. Nanoscale Fabrication of the Ferroelectric Polymer Poly(vinylidene Fluoride with Trifluoroethylene) P(VDF-TrFE) 75:25 Thin Films by Atomic Force Microscope Nanolithography, Scanning, (04 2012): 0. doi: 10.1002/sca.21024
08/08/2013	5.00	William Serrano, Nicholas J. Pinto. Electrospun Fibers of Poly(Vinylidene Fluoride-Trifluoroethylene)/Poly (3-Hexylthiophene) Blends from Tetrahydrofuran, Ferroelectrics, (01 2012): 0. doi: 10.1080/00150193.2012.707830

TOTAL: 4

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received   Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Electrospun fibers of Poly lactic acid/Polyaniline at low polymer concentrations, W. Serrano, A. Mélendez, I. Ramos and N.J. Pinto, American Chemical Society Fall Meeting, San Francisco, CA (August 2014).

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received   Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received		Paper
08/08/2012	3.00	Nicholas Pinto, William Serrano. COMPOSITE NANOFIBERS OF ELECTROACTIVE POLYMERS PREPARED VIA ELECTROSPINNING, 15th European Conference on Composite Materials. 24-JUN-12, . : ,
08/08/2012	4.00	William Serrano, Nicholas Pinto. Electrospun fibers of poly (vinylidene fluoride-trifluoroethylene)/ poly (3-hexylthiophene) blends from tetrahydrofuran, National Conference on Undergraduate Research. 29-MAR-12, . : ,
08/11/2014	7.00	Alexander O. Rosado, Nicholas J. Pinto. Effect of Ultraviolet Irradiation on an n-Doped Semiconductor Thin Film Transistor, . , . : ,
08/11/2014	9.00	Alexander O. Rosado, Nicholas J. Pinto. Dual Input Logic AND Device Fabricated Using an n-doped Semiconductor: Effects of UV Light on Charge Mobility, National Conference on Undergraduate Research. 11-APR-13, . : ,

TOTAL: **4**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
08/07/2012	1.00	William Serrano, Nicholas Pinto. Electrospun fibers of poly(vinylidene fluoride-trifluoroethylene)/poly(3-hexylthiophene) blends from tetrahydrofuran, Ferroelectrics (12 2011)

TOTAL: **1**

Number of Manuscripts:

Books

Received	Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Nicholas Pinto was chosen to be included in the Marquis Who's Who in America

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Kety Jimenez	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Luis Rosa	1.00	
Nicholas Pinto	1.00	
FTE Equivalent:	**2.00**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
William Serrano	1.00	Physics
Eduardo Vega	1.00	Physics
Pablo Sepulveda	0.50	Physics
Stephanie Rodriguez	0.50	Physics
Luis Martinez	0.50	Physics
Fernand Torres	0.50	Physics
FTE Equivalent:	**4.00**	
Total Number:	**6**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 2.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 2.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 4.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 1.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 2.00

Names of Personnel receiving masters degrees

NAME	
Kety Jimenez	
Total Number:	**1**

Names of personnel receiving PHDs

NAME	
Total Number:	

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Please see attached report for accomplishments from May 2011 - July 2014.

For the extension period (August 2014-November 2014) we report the following:

The major scientific accomplishments in this proposal were submitted in the IPR's. During this extension period, the PI worked with High School Students during the summer 2014 and part of the Fall 2014 semester. The accomplishments were thus limited to training these students in the scientific process. Given below is a brief description of the research undertaken by these students.

i)Andy Lopez (11th grade) worked in my lab during the summer 2014, his project was to prepare FET’s and diodes using exfoliated MoS2 thin films. It was difficult at the beginning, but as the summer progressed he was able to get fairly thin films and make the devices.

ii)Faviola Marrero (11th grade) worked on the preparation of PEDOT-PSSA thin films and fibers for alcohol gas sensing. She learned to prepare fibers and films and make a gas sensor. Then she learned to analyze the data and how to calculate response and recovery times and the sensitivity of the sensors.

iii)Victoria Pinto (10th grade) worked on the coaxial electrospinning of polymers with the goal of being able to make hollow fibers. She learned the electrospinning technique and how to make polymer solutions. The she learned how to use the SEM to take images of her fibers.

iv)Mereliz Fuertes (12th grade) worked on making PEDOT-PSSA thin films for use as glucose sensors. She was able to make the sensors and part of the project involved making glucose solutions of different molarity. This work was presented at the local science fair. Mereliz won a prize in the district competition of the science fair and will make in to the regional competition.

v)Maybelline Caban (11th grade) worked on the fabrication of a capacitor using a thin film of PVDF-TrFE as the dielectric. She as successful with using a thin film but the capacitor made from electrospun fibers did not work as there would always be a short between the capacitor terminals. She worked in close collaboration with Pablo who was the expert in the use of the Impedance Analyzer. Maybelline won a prize in the district competition of the science fair and will make in to the regional competition.

Technology Transfer

Scientific Progress and Accomplishments (May 2011 – November 2014)

Summary

Work on this proposal concentrated on studying the following polymers: poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE); poly(3-hexylthiophene) (P3HT); poly(3,4-ethylenedioxthiophene) doped with poly-styrene sulfonic acid (PEDOT-PSSA); and (poly[N,N′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyll-alt-5,5′-(2,2′-bithiophene)]-$[P(ND12OD\text{-}T2)]_{n.}$ We used the Langmuir Blodgett technique to prepare thin films and electrospinning to prepare fine fibers of these polymers. The goal was to make devices and sensors. Using an atomic force microscope we were able to make cuts into the fibers (nano-shaving) and record the current-voltage characteristics of the cut fiber. The results show the onset of an electronic gap as the cuts progress into the fiber. Field effect transistors were also prepared and used as UV sensors and also the device performance improved under UV illumination. The work was carried out by several undergraduate students and one graduate student. Students were involved in many poster presentations at scientific conferences and in refereed publications. State of the art equipment was also purchased making our laboratory competitive for undergraduate institutions. The following report summarizes the various projects that were undertaken over the three year period of this project.

Period May 2011 – July 2012

Electrospun fibers of PVDF-TrFE/P3HT blends

In this project fibers of the ferroelectric poly(vinylidene fluoride-trifluoroethylene) blended with the semiconducting regio-regular poly(3-hexylthiophene) polymer – (PVDF-TrFE/P3HT) were prepared for the first time in air at room temperature using the electrospinning technique that is cheap, fast and reliable. The presence of P3HT assisted in fabrication of PVDF-TrFE fibers at low polymer concentrations in tetrahydrofuran (THF) than currently possible, with the fiber diameters increasing as the concentration of PVDF-TrFE increases. UV/VIS spectroscopy showed that P3HT was uniformly incorporated into the PVDF-TrFE solution with no polymer segregation. Scanning electron microscope images show a reduction in the beading effect and an increase in the quantity of fiber formation when P3HT is incorporated into the solution. Figure 1 shows SEM images of the fibers at various concentrations.

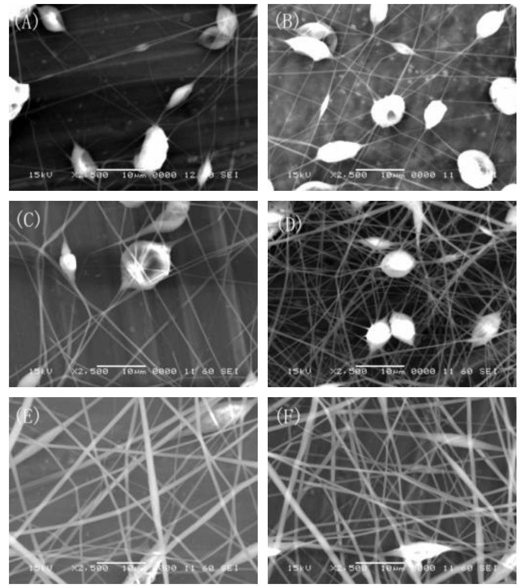
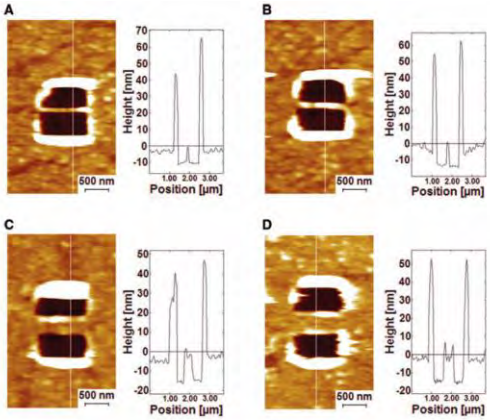
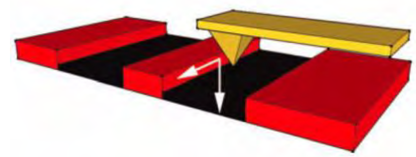


Figure 1: SEM images of electrospun fibers of (a) 7wt% PVF2-TrFE; (b) 7wt% PVF2-TrFE/P3HT; (c) 9wt% PVF2-TrFE; (d) 9wt% PVF2-TrFE/P3HT; (e) 11wt% PVF2-TrFE; (f) 11wt% PVF2-TrFE/P3HT. All images have the same magnification and the scale bar in each represents 10 μm.

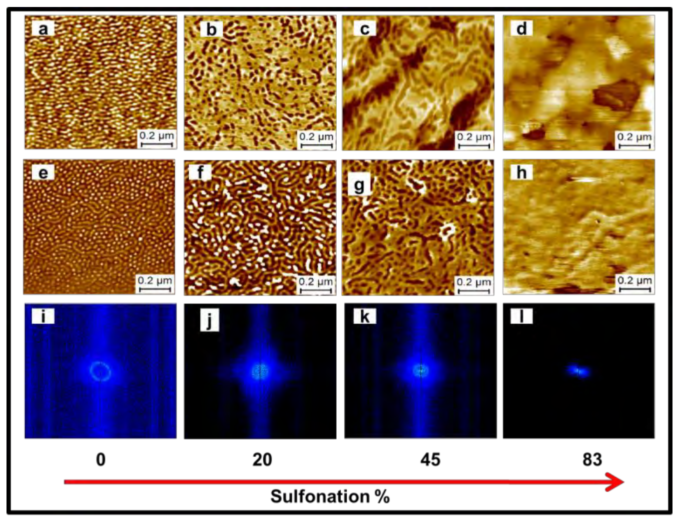
Thin films of PVDF-TrFE via LB technique (Nano shaving)

Thin films of an organic ferroelectric system, poly(vinylidene fluoride with trifluoroethylene) P(VDF-TrFE, Kureha Corporation, Tokyo, Japan) 75:25 layers, have been deposited on highly ordered pyrolytic graphite and silicon dioxide by the horizontal Schaefer method of Langmuir–Blodgett techniques. It is possible to “shave” or mechanically displace small regions of the polymer film by using atomic force microscope nanolithography techniques such as nanoshaving, leaving swaths of the surface cut to a depth of 4 nm and 12 nm exposing the substrate. The results of fabricating stripes by nanoshaving two holes close to each other show a limit to the material “stripe” widths of an average of 153.29 nm and 177.67 nm that can be produced. Due to the lack of adhesion between the substrates and the polymer P(VDF-TrFE) film, smaller “stripes” of P(VDFTrFE) cannot be produced, and it can be shown by the sequencing of nanoshaved regions that “stripes” of thin films can be removed.





Thin films of sulfonated block copolymers are of particular interest for applications in microelectrochemical devices. This study focuses on the fabrication and characterization of sulfonated poly (styrene-isobutylene-styrene) (SIBS) triblock copolymer films. More specifically, the morphological properties are evaluated as a function of processing conditions. For these studies, SIBS thin films are deposited onto silicon wafer substrates via spin-coating and critical parameters such as the sulfonation percent, solvent system, and polymer concentration are evaluated. The effect of a thermal annealing treatment on film morphology is also investigated. A variety of techniques are used for the materials characterization studies including profilometry, atomic force microscopy (AFM), and X-ray diffraction (XRD). Profilometry results show that the film thickness increases as a function of polymer concentration and sulfonation percent. AFM results reveal a morphological transition from spherical domains to a more disordered morphology with interconnected cylinders as the sulfonation percent increases from 0% to 45%. In addition, the polystyrene (PS) domain size also increases as a function of both, sulfonation percent and polymer concentration in the film. Significant effects on the phase-separated morphology are also observed as a result of the thermal annealing treatment.



Conference Presentations

1) *Multifunctional devices based on electrospun PEDOT-PSSA nanofibers*, N.J. Pinto, **Organic Microelectronics & Optoelectronics Workshop VII, July 18-20, 2011, San Francisco, CA.**
2) *Schottky diodes and sensors fabricated from electrospun PEDOT-PSSA nanofibers and their characterization in toxic gaseous environments*, Y. Davila, D. Rivera and N.J. Pinto, **American Chemical Society Meeting, August 29-31, 2011, Denver, CO.**
3) *Nanoscale Fabrication of the Ferroelectric Polymer Poly(Vinylidene Fluoride with Trifluoroethylene) P(VDF-TrFE) 75:25 Thin Films by Atomic Force Microscope Nanolithography*, O. Vega, D. Delgado, F. Wong, R. Gonzalez and L. Rosa, **Materials Research Society Fall 2011 meeting, Boston, MA.**
4) *Electrical characterization of field effect transistors made from C-nanotubes covered with poly(3-hexylthiophene)*, L. Pomales, N.J. Pinto, M. Lerner, A.T. Johnson, **American Physical Society, Annual March Meeting, Boston, MA (February 2012).**
5) *Electrical characterization of CVD graphene*, Y. Dávila, N.J. Pinto, Z. Lou, A.T. Johnson, **American Physical Society, Annual March Meeting, Boston, MA (February 2012).**
6) *Fabrication and characterization of poly (vinylidene fluoride-trifluoroethylene)/ poly (3-hexylthiophene) (PVDF-TrFE/P3HT) nanofibers via electrospinning*, W. Serrano, N.J. Pinto, **National Conference on Undergraduate Research (NCUR), Ogden, UT (March 2012).**
7) *Composite nanofibers of electro-active polymers prepared via electrospinning*, N.J. Pinto, W. Serrano, **15th European Conference on Composite Materials, Venice, Italy (June 2012).**
8) *Dip Pen Nanolithography Using a Polyacrylonitrile Based Ink*, O. V. Manzano, G. J. P. Medina, R. Furlana, A. N. R. da Silvab, and L. G. Rosa, **Poster presentation at the annual meeting of the Institute of Functional Materials, Puerto Rico (2011)**.

Refereed Publications:

1) *Electrospun fibers of poly(vinylidene fluoride-trifluoroethylene)/poly(3-hexylthiophene) blends from tetrahydrofuran*, W. Serrano and N.J. Pinto, *Ferroelectrics* – DOI 10.1080/00150193.2012.707830 (in print 2012).
2) *Nanoscale Fabrication of the Ferroelectric Polymer Poly(vinylidene Fluoride with Trifluoroethylene) P(VDF-TrFE) 75:25 Thin Films by Atomic Force Microscope Nanolithography*, O. Vega, D. Delgado, F. Wong, R. Gonzalez, L.G. Rosa *SCANNING,* DOI: 10.1002/sca.21024, (2012).
3) *Fabrication and Morphological Characterization of Sulfonated Poly(Styrene-Isobutylene-Styrene) Triblock Copolymer Thin Films*, O.A. Movil-Cabrera, O. Vega, L.

G. Rosa and A.M. Padovani, *Polymer Science: Polymer Physics*, accepted for publication, (2012).

4) *Composite nanofibers of electroactive polymers prepared via electrospinning*, N.J. Pinto and W. Serrano, *Conference Proceedings* (15^{th} European Conference on Composite Materials).
5) *Electrospun fibers of poly (vinylidene fluoride-trifluoroethylene)/ poly (3-hexylthiophene) blends from tetrahydrofuran*, W. Serrano and N.J.Pinto, *Conference Proceedings* (2012 National Conference on Undergraduate Research - Ogden, UT).

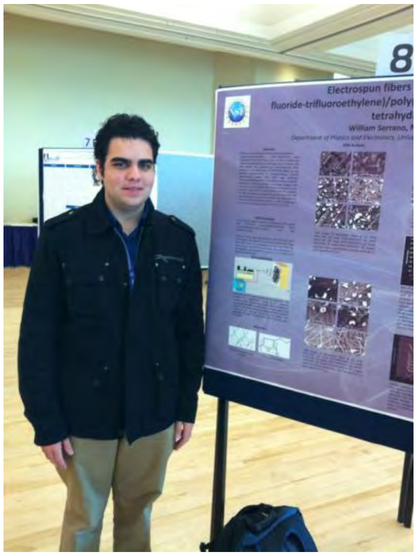
Manuscripts under preparation

1) O. Vega, E. Vega, J.P. Cordova and L.G. Rosa, "Transport Characterization and Electron Localization on PDOT Nanoribbons: AFM Nanofabrication and Lithography" (2012)
2) K. Jimenez, J. Alvira, J. Luciano and L.G. Rosa, "Structure characterization and stress shearing effects on the organic ferroelectric polymer P(VDF-TrFE)" (2012)
3) F. Wong, D. Colon, G. Perez, M. Bonilla and L.G. Rosa, "Band bending on polymer blens of the organic semiconducting polymer P3HT and the organic ferroelectric" (2012).
4) A. Rosado, N.J. Pinto, "Effects of UV irradiation on the *n*-doped semiconductor poly[N,N′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyll-alt-5,5′-(2,2′-bithiophene)]" (2012).

Summer 2012 REU Programs

William Serrano and Eduardo Vega who are undergraduates at UPRH and were funded by this DoD program, spent the summer in research programs in the US. William went to Penn State University and Eduardo went to the University of Nebraska. Such programs are very useful for the students who gain additional research experience and are able to work in a real research environment compared to the undergraduate research facilities that we provide at UPRH. We hope that this will further motivate them to seek graduate studies in STEM areas after they graduate.

Photo Gallery of DoD supported students



William Serrano, a second year undergraduate student, presents his poster at the annual National Conference on Undergraduate Research at Ogden, UT in March 2012. He worked on the fabrication of PVDF-TrFE/P3HT fibers and their characterization. He has published one paper in the NCUR conference proceedings and another paper has been accepted for publication in the journal *Ferroelectrics*.

Eduardo Vega is a second year undergraduate student who is working on making electrical connections to PEDOT nanoribbons.

Kety Jimenez is a first year graduate student and is seen working on the thermal evaporator to deposit electrodes on ferroelectric capacitors.

Period August 2012 – July 2013

Nanoshaving a PEDOT-PSSA nanoribbon

In this project, a nanoribbon having a width of ~2□m and thickness of 10nm was electrospun on a doped Si/SiO_2 wafer using electrospinning. The lengths of these ribbons were several 100□m long. A transmission electron microscope grid was placed on an isolated ribbon and used as a template to define electrodes along its length. After evaporating 100nm Au, the grids were removed and external connections were made to the fiber. Using an electrometer the current through the fiber was measured after an atomic force microscope (AFM) was used to make small cuts to the ribbon in a direction perpendicular to the ribbon length. Each successive cut led to the effective ribbon width being reduced at the location of the cut and hence will affect the current flowing there. Prior to the cuts, the I-V curve was Ohmic as is expected for a conducting polymer like PEDOT-PSSA. However when the width is reduced sufficiently approximating the size of the metallic granular islands in the polymer, the characteristic curve begins to deviate from linearity and shows the opening of an electronic gap in the polymer. This is an indication that the polymer is shifting away from being metallic to now exhibiting semiconducting properties. Figure 1 on the next page shows the cuts being made to the fiber and the corresponding I-V curves. It is a dynamic figure that if you le douclick on it, it will show you the progressive cuts and the corresponding IV curves.

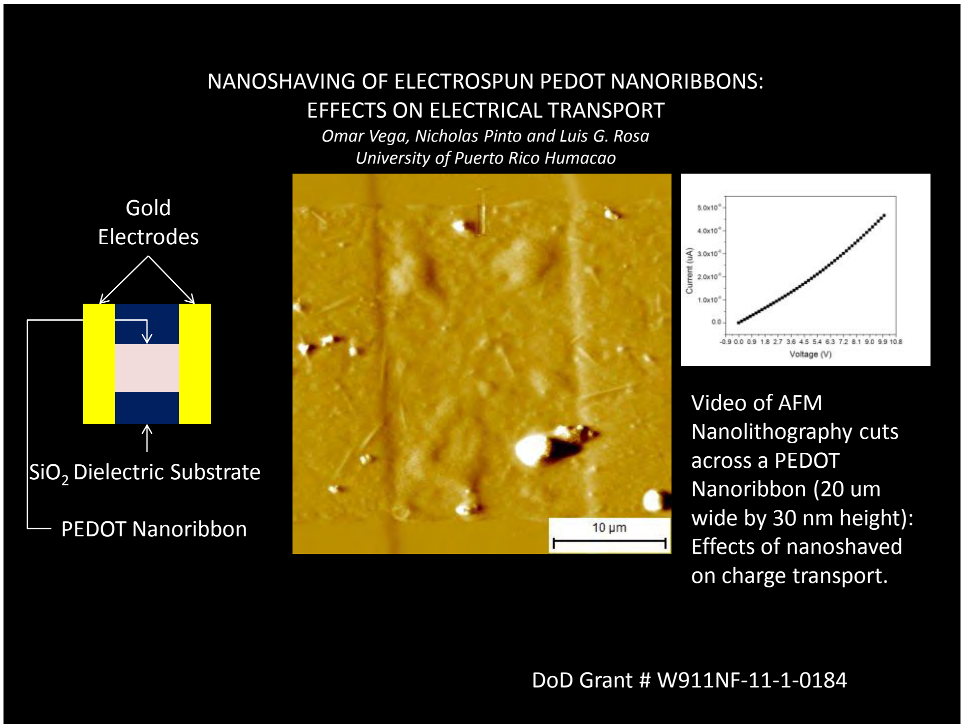


Figure 1: The figure above is a dynamic photograph of cuts being made to the ribbon using an AFM perpendicular to its length and the corresponding IV curve for each cut. The ribbon is lying in between the two parallel lines. Double click on the figure to see the action.

Effect of UV illumination on an *n*-doped field effect transistor

In this project, the goal was to make FET's based on *n*-doped polymer $[P(ND12OD\text{-}T2)]_n$ which is air stable. The first step was to be able to electrospin fibers which we were able to do and then to connect a single fiber in a FET configuration. Figure 2 shows a SEM image of the fibers. These fibers appeared rough but continuous. The diameters of these fibers were in the range in 0.5 – 10 μm. These fibers were electrospun from $CHCl_3$ and had lengths that were several cm long. Individual fibers were captured on doped Si/SiO_2 wafers and connected in a field effect transistor configuration. The device was characterized in vacuum under ambient illumination and under exposure to UV (λ=365nm) light. Figure 3 shows the plot of the drain-source current (I_{DS}) as a function of drain-source voltage (V_{DS}) of a [P(ND12OD-T2] spin coated thin film FET at various gate-source biases (V_{GS}) in the absence and presence of UV irradiation. Fibers are also being investigated. At zero gate bias, the measured channel currents were relatively small (in the pA range) but with increasing positive gate bias, the channel currents increase linearly for low V_{DS} with a channel resistance of 260MΩ at V_{GS}=70Vand then saturate for $V_{DS} >$ 20V. The saturation in I_{DS} combined with increasing channel current for larger positive gate bias imply that the device operates as a FET and that the majority charge carriers are electrons as expected for this *n*-doped semiconductor material. Also, as seen in this figure, in the presence of UV irradiation, the channel currents are always higher for a given V_{GS} and V_{DS}, implying increased device on/off ratio and charge mobility. This increase in channel current is most likely due to a resonance effect at 365nm (photo-excitation) and also due surface charge doping which results from desorption of electron trapping species. The highlights of this research are the following:

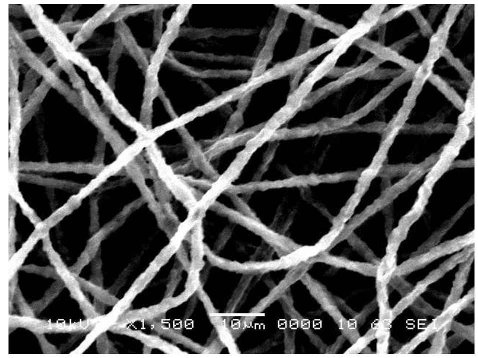


Figure 2: Electrospun $[P(ND12OD\text{-}T2)]_n$ fibers

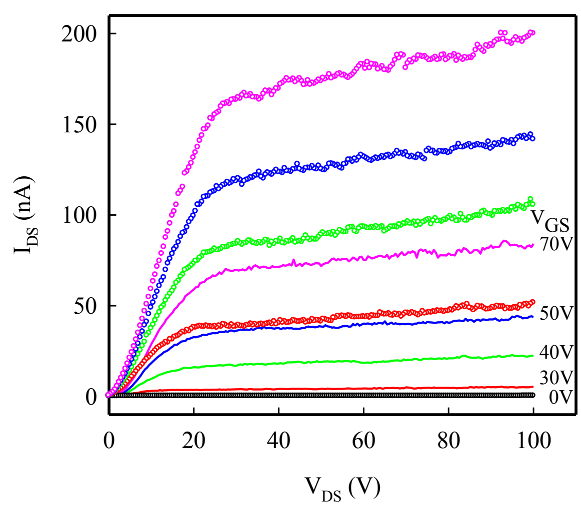


Figure 3: Drain-source current (I_{DS}) vs. drain-source voltage (V_{GS}) for a thin film [P(ND12OD-T2] FET in vacuum and at room temperature for various gate-source (V_{GS}) biases. The solid lines represent data taken in the absence of UV and the symbols correspond to data taken during UV exposure. Similar colors correspond to similar V_{GS} values.

- UV irradiation leads to an increase in the charge mobility and device on/off ratio.
- UV irradiation shifts the threshold voltage towards negative values suggesting *n*-type doping in the process.
- The device can also be used as a UV light sensor with a response time of ~20 s making it multifunctional.
- The device is reusable with no adverse effects due to the UV irradiation.

- UV irradiation can improve device parameters without the need for cumbersome chemical purification.

Refereed publications:

1. Electrospun fibers of poly(vinylidene fluoride-trifluoroethylene)/poly(3-hexylthiophene) blends from tetrahydrofuran, W. Serrano and N.J. Pinto, *Ferroelectrics* **432:1**, 41-48 (2012).

2. Dip Pen Nanolithography Using a Polyacrylonitrile Based Ink, Omar Vega, Godohaldo Perez, Rogerio Furlan, Anna da Silva and Luis G. Rosa, *ECS Transactions*, **49 (1)**, 241, (2012).

3. Nanoscale Fabrication of the Ferroelectric Polymer Poly(vinylidene fluoride with trifluoroethylene) P(VDF-TrFE) 75:25 Thin Films by Atomic Force Microscope Nanolithography, Omar Vega, David Delgado, Freddy Wong, Rosette Gonzalez, Luis G. Rosa, *Scanning*, **34**, 404, (2012).

4. Electrospun fibers of $[P(ND12OD\text{-}T2)]_n$ on p-doped Si: Fabrication of a sub-micron size *p-n* junction diode, A.O. Rosado and N.J. Pinto, *Int. J. of Chem. Engg.* (Accepted 2013).

5. Stress Shearing Effects on the Polarization of the Organic Ferroelectric Polymer Kety Jimenez, Omar Vega, Jeileen Luciano, Fernand Torres and Luis G. Rosa, *Master Thesis* of Kety Jimenez (2013).

6. Kong Linmei, Lucie Routaboul, Pierre Braunstein, Hong-Gi Park, Jaewu Choi, John P. Cordova, Eduardo Vega, Luis G. Rosa, Bernard Doudine and Peter Dowben, "Adsorption of TCNQH-functionalized quinonoid zwitterions on gold and grapheme: evidence for dominant intermolecular interactions", *RSC Advances*, 3 (27), 10956, (2013).

Conference Presentations:

1. Electrospun conducting polymer nanofibers as the active material in sensors and diodes, N.J. Pinto, Invited talk, **8th Ibero-American Congress on Sensors-Ibersensor2012, Isla Verde, Puerto Rico, October 2012.**
2. Devices and sensors based on PVDF-TrFE/SWCNT's composites, M. Bonilla, I. Ramos and N.J. Pinto, **8th Ibero-American Congress on Sensors-Ibersensor2012, Isla Verde, Puerto Rico, October 2012.**
3. Electrospun fibers of PLA/P3HT blends for device and sensor applications, W. Serrano, N.J. Pinto, **Annual March Meeting, Baltimore, MD (March 2013).**
4. *p-n* junction diodes fabricated from isolated electrospun fibers of (P(NDI2ODT2)) and an inorganic *p*-doped semiconductor, A. Rosado, N.J. Pinto, **Annual March Meeting, Baltimore, MD (March 2013).**
5. CVD graphene as a glucose sensor, M. Bonilla, N.J. Pinto, M. Lerner, G. Hee and A.T. Johnson Jr., **48th Puerto Rico Junior Technical Meeting, Gurabo, PR (March 2013).**

6. Effect of Toluene wash on the electronic properties of CVD Graphene, M. Oquendo, N.J. Pinto, G. Hee and A.T. Johnson Jr., **48th Puerto Rico Junior Technical Meeting, Gurabo, PR (March 2013).**
7. Electrospun fibers of PLA/P3HT blends for device and sensor applications, W. Serrano and N.J. Pinto, **48th Puerto Rico Junior Technical Meeting, Gurabo, PR (March 2013).**
8. Dual input logic AND device fabricated using an n-doped semiconductor: Effects of UV light on charge mobility, A. Rosado, N.J. Pinto, **National Conference on Undergraduate Research (NCUR), La Crosse, WI (April 2013).**

The following presentations were made at WhoPhy 2012 (WhoPhy is a conference for woman and minorities in Physics held in the University of Nebraska every year). Students where supported by DoD funds for this trip

- Nanoscale Fabrication of the Ferroelectric Polymer PVDF Thin Films by AFM Rosette Gonzalez.
- Stress Shearing Effects on the Polarization of the Organic Ferroelectric Polymer, Kety Jimenez and Jeileen Luciano.
- Band Bending in Spin Crossover Molecule /PVDF-TrFE by Poling the Ferroelectric Component, Eduardo Vega.
- Using X-Ray photo-electron spectroscopy (XPS) to Identify Oxidation States and Theta Ratios CeO_2, Fernand Torres.
- Dip Pen Nanolithography of PAN (Polyacrylonitrile) for patterned carbon nanotubes, Omar Vega.

Manuscripts under review/preparation

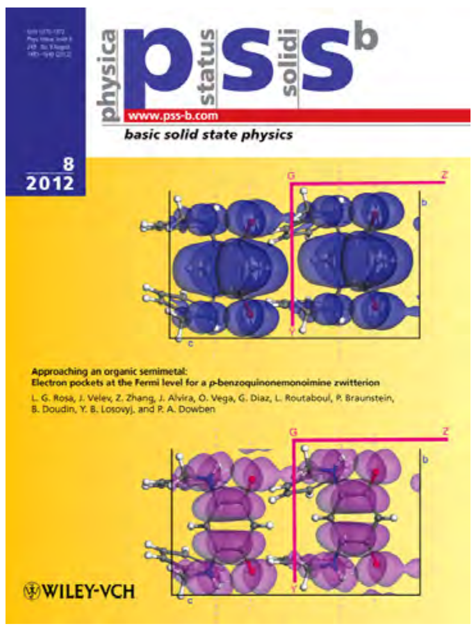
1) Effect of ultraviolet irradiation on an *n*-doped semiconductor thin film transistor, A.O. Rosado and N.J. Pinto, Submitted to *ACS Polymer preprints*. **Paper# 206** to be presented at the American Chemical Society Meeting in Indianapolis, IN, in September 2013.
2) Dual Input Logic A.N.D. Device Fabricated Using an *n*-doped Semiconductor: Effects of UV Light on Charge Mobility, A.O. Rosado and N.J. Pinto, Submitted to the 2013 *National Conference of Undergraduate Research Conference Proceedings*.
3) Changing Molecular Band Offsets in Polymer Blends of (P3HT/PVDF-TrFE) due to Ferroelectric Poling in Nonvolatile Memory Devices, Freddy Wong, Godohaldo Perez, Manuel Bonilla, Juan A. Colon-Santana, Xin Zhang, Pankaj Sharma, Alexei Gruverman, Peter A. Dowben and Luis G. Rosa, *RSC Advances (under review)*.
4) Fabrication and Morphological Characterization of Sulfonated Poly(Styrene-Isobutylene-Styrene) Triblock Copolymer Thin Films, O.A. Movil-Cabrera, O. Vega, L. G. Rosa and A.M. Padovani, *Polymer Science: Polymer Physics (under review)*.

2013 Summer Research Opportunities

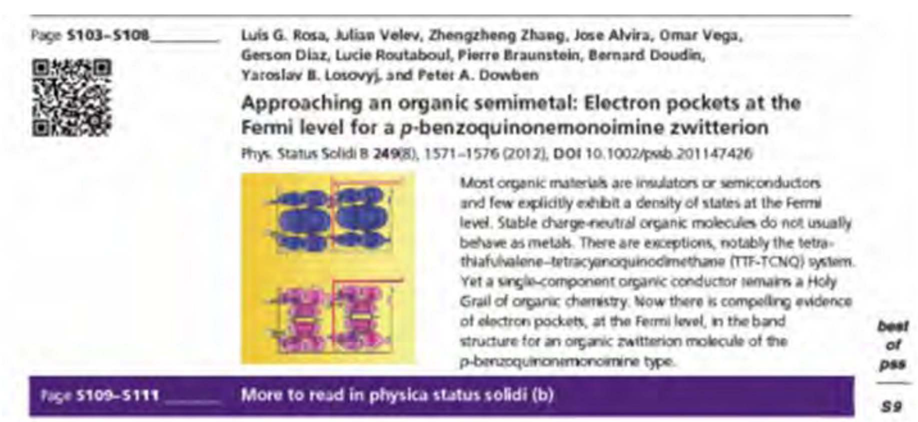
During the summer, three undergraduate students who were part of this project went to REU programs in the US mainland. William Serrano spent the summer at the University of Nebraska-Lincoln, Alexander Rosado spent the summer at the University of Pennsylvania and Eduardo Vega spent the summer at Princeton. These summer internships are an important part of their undergraduate research experiences and will no doubt help them in seeking advanced degrees in Science and Engineering. Kety Jimenez is the only graduate student funded by DoD in this proposal and she has submitted her Master's thesis and is preparing to defend it later this year.

Awards received

1) Omar Vega who is a student in Prof. Rosa's group, won the first prize at the WhoPhy conference for woman and minorities in Physics held in the University of Nebraska every year.
2) Prof. Rosa's paper was showcased on the cover of the journal Physica Status Solidi for 2013.



Prof. Rosa's cover page article became best article for the journal Physics Status Solidi for 2013.



Page S103–S108

Luis G. Rosa, Julian Velev, Zhengzheng Zhang, Jose Alvira, Omar Vega, Gerson Diaz, Lucie Routaboul, Pierre Braunstein, Bernard Doudin, Yaroslav B. Losovyj, and Peter A. Dowben

Approaching an organic semimetal: Electron pockets at the Fermi level for a *p*-benzoquinonemonoimine zwitterion

Phys. Status Solidi B **249**(8), 1571–1576 (2012), DOI 10.1002/pssb.201147426

Most organic materials are insulators or semiconductors and few explicitly exhibit a density of states at the Fermi level. Stable charge-neutral organic molecules do not usually behave as metals. There are exceptions, notably the tetrathiafulvalene–tetracyanoquinodimethane (TTF-TCNQ) system. Yet a single-component organic conductor remains a Holy Grail of organic chemistry. Now there is compelling evidence of electron pockets, at the Fermi level, in the band structure for an organic zwitterion molecule of the p-benzoquinonemonoimine type.

Page S109–S111 More to read in physica status solidi (b)

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S9

Photo gallery of DoD supported students

Students at the WhoPhy 2012. Omar Vega (right) was the winner in a poster contest (2013).

Photograph of a class 100 clean room at UPR-Humacao. DoD funds were used to purchase electronic equipment for this lab (2013).

William Serrano (a senior) using the electrospinning apparatus for polymer fiber fabrication (2013).

Kety Jimenez (a second year graduate student) in the clean room with the thermal evaporator (2013).

Period August 2013 – July 2014

Electrospun PEDOT-PSSA nano-ribbons: Effect of nano-shaving on the device characteristics

PEDOT-PSSA is a commercially available conducting polymer. Using the electrospinning technique, we prepared nano-ribbons of this polymer. In this project, a nano-ribbon having a width of ~2 μm and thickness of 10nm was electrospun on a doped Si/SiO_2 wafer using electrospinning. The lengths of these ribbons were several 100 μm long. A transmission electron microscope grid was placed on an isolated ribbon and used as a template to define electrodes along its length. After evaporating 100nm Au, the grids were removed and external connections were made to the fiber. Using an electrometer the current through the fiber was measured after an atomic force microscope (AFM) was used to make small cuts to the ribbon in a direction perpendicular to the ribbon length. Each successive cut led to the effective ribbon width being reduced at the location of the cut and hence will affect the current flowing there. Prior to the cuts, the I-V curve was Ohmic as is expected for a conducting polymer like PEDOT-PSSA. However when the width is reduced sufficiently approximating the size of the metallic granular islands in the polymer, the characteristic curve begins to deviate from linearity and shows the opening of an electronic gap in the polymer. This is an indication that the polymer is shifting away from being metallic to now exhibiting semiconducting properties. Figure 1 on the next page shows the cuts being made to the fiber and the corresponding I-V curves. It is a dynamic figure that if you double click on it, it will show you the progressive cuts and the corresponding I-V curves. A manuscript based on this work is in progress.

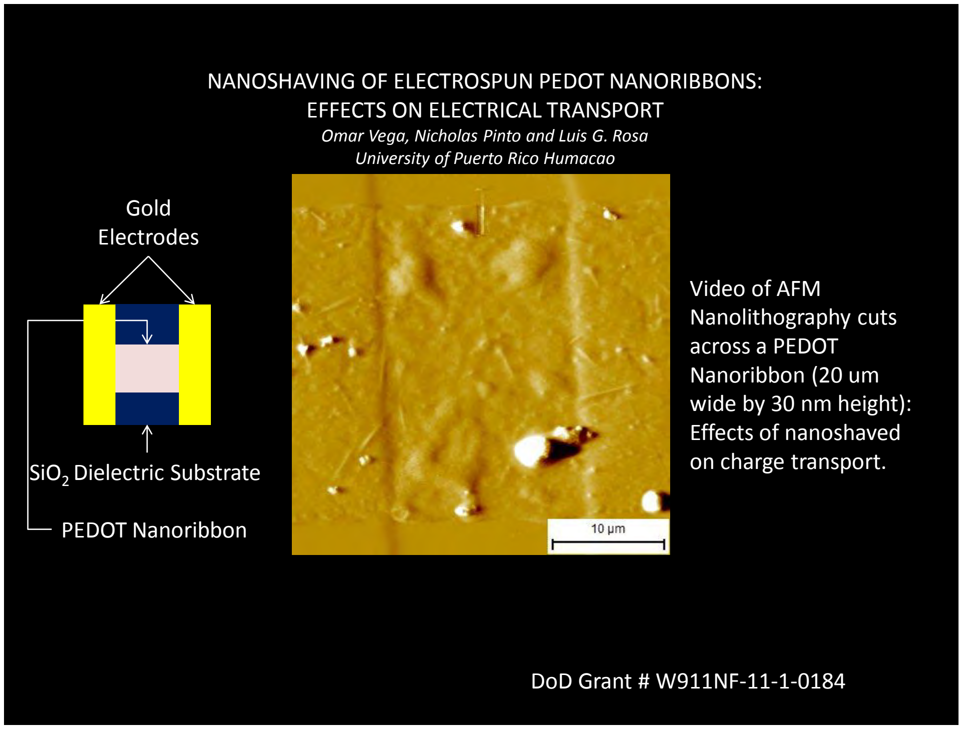


Figure 1: Double click the image to see a movie of the AFM nano-shaving of PEDOT-PSSA. Each cut is 2μm long x 500 nm wide x 30 nm deep.

Dielectric spectroscopy of [P(ND12OD-T2]$_n$

This was a project carried out by Pablo Sepulveda, a second year undergraduate student. Poly[N,N′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyll-alt-5,5′-(2,2′-bithiophene)]-[P(ND12OD-T2)]$_n$ is a *n*-doped polymer that is stable in air. In this work, we have performed the *first* study on the low frequency complex impedance of [P(ND12OD-T2)]$_n$ thin films at room temperature. Analysis of the data showed a relaxation mechanism that is almost Debye like. Exposure to ultra-violet (UV) radiation however led to a decrease of the impedance strength with faster relaxation times and a shift away from the Debye like relaxation mechanism with a slight distribution in relaxation times. These results imply that the presence of UV resulted in a charge increase in the bulk polymer that is related in part to photo-absorption and due to desorption of adsorbed electron trapping species like H_2O^- and O_2^-. The increased charge is equivalent to doping the polymer and allows for the presence of multiple paths for the system to relax. A consequence of this effect should be enhanced mobility due to increased polymer conductance and reduced scattering by the trapped species. By fabricating and testing a field effect transistor (FET) based on this polymer we show that under the same UV radiation, the mobility increased and that there was a shift in the threshold voltage toward negative gate bias implying *n*-doping, consistent with dielectric spectroscopy measurements. Based on these results, UV irradiation, with no post processing, is proposed as a viable method to improve the mobility in this *n*-type polymer and increase its potential for use in high frequency applications.

Figure 2 shows the frequency dependence of the real (ε') part of the complex dielectric permittivity at room temperature with and without UV irradiation. ε' is relatively constant below 1 kHz as is typical for conducting polymers, while above 1 kHz there is a decrease resulting from the onset of freezing of the effective dipoles, representing their inability to follow the variations in the electric field within the sample at higher frequencies. After UV illumination for 35 minutes, there is an increase in ε' suggesting an increase in the charge within the polymer, and turning off the UV brings the polymer to its original condition making it a reversible process. The current increase is understandable when one observes the UV absorption spectra of $[P(ND12OD\text{-}T2)]_n$. The inset to Figure 2, shows the absorption spectra of a thin cast film of $[P(ND12OD\text{-}T2)]_n$ and show two main absorptions located at 380 nm and 670 nm consistent with other reports where the absorption band at 380 nm is suggested to have π-π* character and the higher absorption at 670 nm is related to the highest occupied molecular orbital-lowest unoccupied molecular orbital transition of the polymer. Part of the increase in the charge under UV illumination is therefore a result of the photo-excitation at 380 nm being very close to that of the UV wavelength used in our experiment. Being electronic in nature, this is expected to be a fast and reversible process. We also suggest that in the presence of UV, there is an electron-hole pair generated within the bulk of the polymer. The hole is then attracted to electron trapping species (recombination) like H_2O^- and O_2^- (i.e. $h^+ + O_2^- \rightarrow O_2$gas) removing them from the polymer film reducing scattering and donating the electron which contributes to the observed current increase and leads to *n*-type doping. Such generation and recombination processes are slow and the current increase should be observable in low frequency dielectric permittivity measurements as seen in Figure 2.

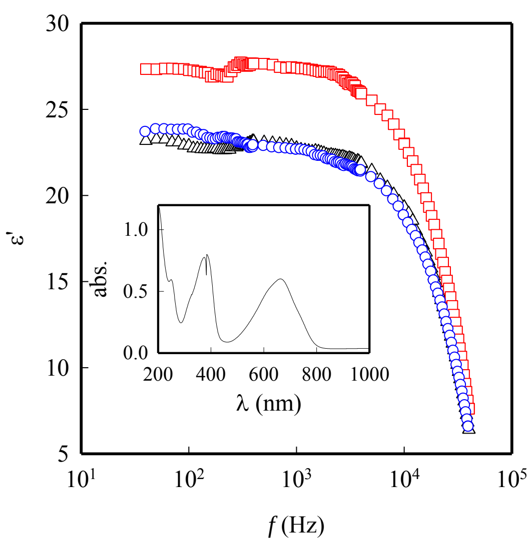


Figure 2: Frequency dependence of the real part of the dielectric permittivity (ε') of the *n*-type polymer $[P(ND12OD\text{-}T2)]_n$: (Δ) before UV radiation; (□) after 35 min of UV radiation; (○) after the UV radiation was turned off. Inset: UV/VIS absorption spectrum of a thin film of spun coated $[P(ND12OD\text{-}T2)]_n$ on a quartz slide.

Refereed publications:

1. Electrospun fibers of $[P(ND12OD\text{-}T2)]_n$ on p-doped Si: Fabrication of a sub-micron size p-n junction diode", A.O. Rosado and N.J. Pinto, *Int. J. of Chem. Engg.* (Serials Publications) **6(2)**, 175-181 (2013).
2. Effect of ultraviolet irradiation on an n-doped semiconductor thin film transistor, A.O. Rosado and N.J. Pinto, *PMSE Preprints* **109**, 1 (2013).

3. Dual Input Logic AND Device Fabricated Using an n-doped Semiconductor: Effects of UV Light on Charge Mobility, A.O. Rosado and N.J. Pinto, *National Conference on Undergraduate Research, Conference Proceedings* **(2013)**.

4. Dielectric spectroscopy of $[P(NID2OD\text{-}T2)]_n$ thin films: Effects of UV radiation on charge transport, P.I. Sepulveda, A.O. Rosado and N. J. Pinto, *Thin Solid Films* **565**, 300-303 (2014).

5. Changing Molecular Band Offsets in Polymer Blends of (P3HT/PVDF-TrFE) due to Ferroelectric Poling in Nonvolatile Memory Devices, Freddy Wong, Godohaldo Perez, Manuel Bonilla, Juan A. Colon-Santana, Xin Zhang, Pankaj Sharma, Alexei Gruverman, Peter A. Dowben and Luis G. Rosa, *RSC Advances* **4 (6)**, 2904-2911 (2014).

6. Kety Jimenez, Omar Vega, Jeileen Luciano, Fernand Torres and Luis G. Rosa, "Stress Shearing Effects on the Polarization of the Organic Ferroelectric Polymer" *Master Thesis* of Kety Jimenez (2014).

7. The spin state of a molecular adsorbate driven by the ferroelectric substrate polarization" X. Zhang, T. Palamarciuc, J.-F. Létard, P. Rosa, E. Vega, F. Torres, L.G Rosa, B. Doudin, P.A Dowben, *Chemical Communications*, **50(18)**, 2255 (2014).

Conference Presentations:

1. Effect of ultraviolet irradiation on an n-doped semiconductor thin film transistor, A. Rosado and N.J. Pinto, **American Chemical Society Fall Meeting, Indianapolis, IN (September 2013).**

2. Charge transport in CVD graphene with and without a silver coating, M. Oquendo, J. Vedrine, A.T. Johnson Jr. and N.J. Pinto, **49^{th} ACS Junior Technical Meeting, Cayey, PR (March 2014).**

3. Dielectric characterization of the n-doped polymer [P(NID2OD-T2)], P. Sepulveda and N.J. Pinto, **49^{th} ACS Junior Technical Meeting, Cayey, PR (March 2014).**

4. Electrospun fibers of poly(vinylidene fluoride-trifluoroethylene)/[P(NDI2OD-T2)] composites, C. Vazquez and N.J. Pinto, **49th ACS Junior Technical Meeting, Cayey, PR (March 2014).**

5. Charge transport in CVD graphene with and without a silver coating, M. Oquendo, J. Vedrine, A.T. Johnson Jr. and N.J. Pinto, National Conference on Undergraduate Research, NCUR2014, Lexington KY (**April, 2014**).

6. Dielectric characterization of the *n*-doped polymer [P(NID2OD-T2)], P. Sepulveda and N.J. Pinto, National Conference on Undergraduate Research, NCUR2014, Lexington KY (**April, 2014**).

7. Electrospun fibers of poly(vinylidene fluoride-trifluoroethylene)/[P(NDI2OD-T2)] composites, C. Vazquez and N.J. Pinto, National Conference on Undergraduate Research, NCUR2014, Lexington KY (**April, 2014**).

8. Electrospinning of electro-active materials: Devices based on crossed nanofibers, N.J. Pinto, Invited Talk presented at the workshop **"Electrospinning for high performing sensing", Monterotondo, Rome, Italy (April 29-30, 2014).**

9. Back gate tunable diode fabricated from a hetero-junction of an electrospun PEDOT-PSSA nano-ribbon and multilayer MoS_2, C. Vazquez and N.J. Pinto, *22nd International Conference for Science and Technology of Synthetic Metals* (ICSM2014), **Turku, Finland (June 2014)**.

10. Transport Properties and Cross section Dependence on PEDOT (Poly (3, 4-ethylenedioxythiophene)) Nanoribbons, O. Vega, J. Luciano, E. Vega, N. Pinto, L Rosa Bulletin of the American Physical Society, **American Physical Society March Meeting (2014)**.

11. Band structure and device fabrication using thin-films of p-benzoquinonemonoimine zwitterion/P3HT blends, G. Diaz, F. Wong, E. Vega, L. Rosa, Bulletin of the American Physical Society, **American Physical Society March Meeting (2014)**.

12. Band Bending in Polymer Blends of PVDF-TrFE/P3HT by Poling the Ferroelectric Component, F. Wong, G. Perez, M. Bonilla, D. Colon, J. Colon, I. Ketsman, A. Gruverman and Luis G. Rosa Bulletin of the American Physical Society, **American Physical Society March Meeting (2014)**.

WhoPhy 2013 http://wophy.unl.edu/ **(WhoPhy is a conference for woman and minorities in Physics held in the University of Nebraska every year).**

1. Intrinsic and Extrinsic Parameter and their Role in Optical Sensors Calibration, Stephanie Rodriguez

2. Effects of Aggressive Environment in the Properties of Graphene, Christian Laboy
   Fabrication of Nanopillar by Nanosphere Lithography, Jose Santana

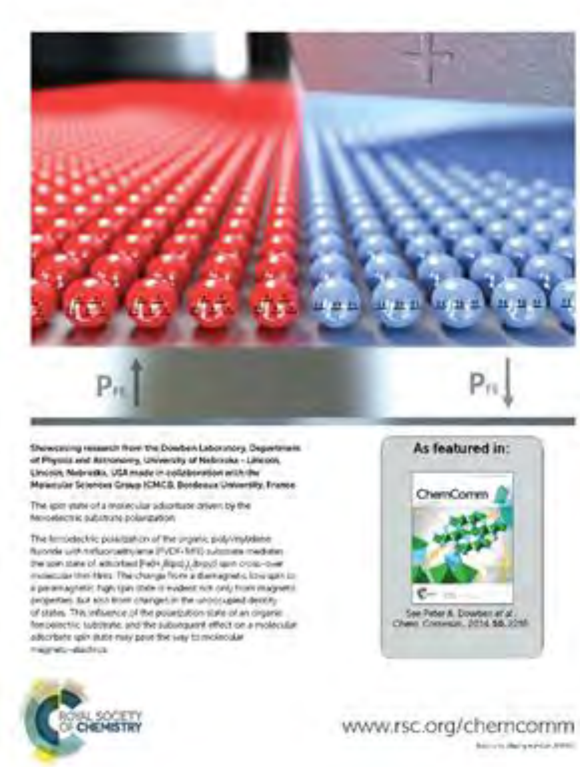
Manuscripts under review/preparation

1. Omar Vega, Nicholas Pinto and Luis G Rosa "Nano-shaving on PEDOT nano-ribbons: Electrical Transport Properties" Under Preparation (2014).

2014 Summer Research Opportunities and students who have graduated.

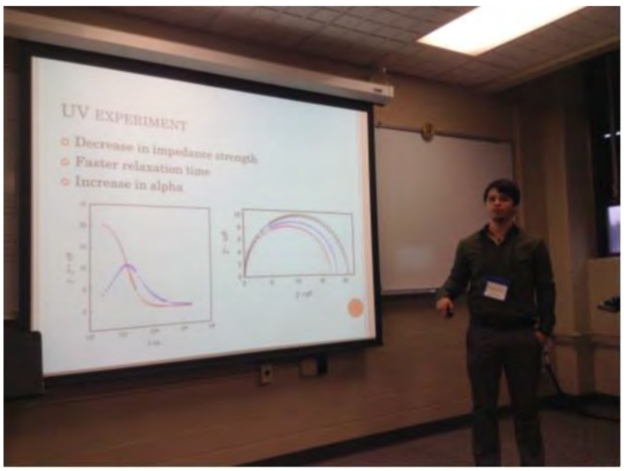
During the summer, three undergraduate students who were part of this DoD funded project went to REU programs in the US mainland. William Serrano spent the summer at NIST in Maryland, Pablo Sepulveda spent the summer at Penn State University, Luis Martínez spent the summer at the University of South Florida. These summer internships are an important part of their undergraduate research experiences and will no doubt help them in seeking advanced degrees in Science and Engineering. Eduardo Vega who was also funded with DoD funds graduated with a BS in Physics at UPR-Humacao and is currently a graduate student at Wesleyan University in the Physics PhD program. Kety Jiménez was the only graduate student funded in this DoD project who has now graduated with a MS in Physics and is currently a Full Professor at the Autonomous University of Dominican Republic.

The photograph below is the cover page of the journal Chemical Communications where Prof. Rosa has published an article with his student Eduardo Vega

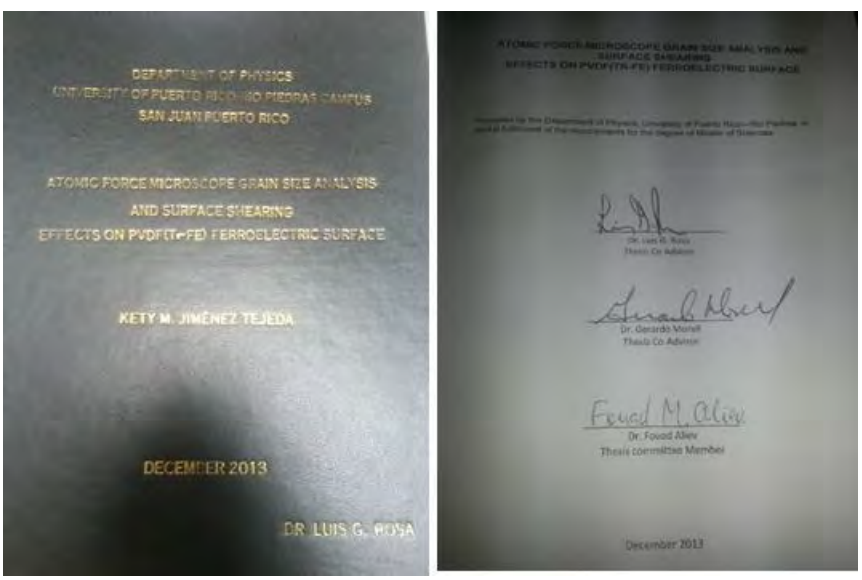


“The spin state of a molecular adsorbate driven by the ferroelectric substrate polarization”
Xin Zhang, Tatiana Palamarciuc, Jean-François Létard, Patrick Rosa, ***Eduardo Vega Lozada, Fernand Torres***, ***Luis G Rosa***, Bernard Doudin, Peter A Dowben, Chemical Communications, 50(18), 2255, (2014).

Picture Gallery



Pablo Sepulveda presents his talk at the NCUR in Lexington, KY, April 3-5, 2014.



Kety Jimenez (Masters of Physics Graduate Program, Senior) Graduated from Master Degree Fall 2013. Currently she is a Full Professor at Autonomous University of Dominican Republic. An image of her thesis is shown above.

Period August 2014 – November 2014

During this final period we continued research on conducting and non-conducting polymer nanofibers. Five High School students worked with me during the Summer 2014 and part of the Fall 2014 semester. Most of their research was related to conducing, non-conducting polymers and MoS_2. Their work mainly consisted in sample preparation, running the experiments and simple data analysis. Two of these students particpated in the High School Science Fairs. The goal was to motivate these students to do some basic research and to choose a career in Science upon graduating from High School.